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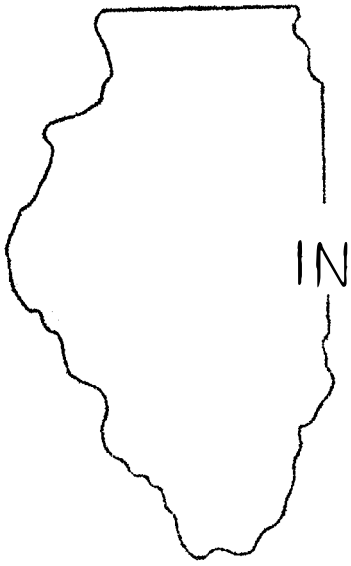

INDUSTRIAL MINERALS NOTES 31

CLAYS AS BINDING MATERIALS

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A B S T R A C T

The uses of different types of clay for binders in a variety of applications are described briefly in this report.

The information was obtained from approximately 125 abstracts published since 1937 in Chemical Abstracts and in American Ceramic Abstracts, and since 1950 in British Ceramic Abstracts.

CLAYS AS BINDING MATERIALS

INTRODUCTION

A wide variety of materials have found application as binders for the manufacture of pellets and briquets. The Illinois State Geological Survey published Industrial Minerals Notes No. 19, "Binding Materials Used in Making Pellets and Briquets," in November 1964 listing many of these.

That report mentioned briefly the use of clays as binders, but did not attempt to cover the field, which is a rather large one.

The present summary has been prepared to assemble this information for use within the Illinois Geological Survey, and for other interested workers.

This compilation is based largely on a search of Chemical Abstracts indexes from 1937 through the first half of 1965, but has been supplemented by similarly searching American Ceramics Abstracts, January 1937 through August 1966, and British Ceramics Abstracts, January 1950 through November 1965. Although one or two more recent references have been included, coverage has not been systematic or complete for publications issued since the dates given above because indexes were not available at the time the search was being made.

It should be noted that the rather meager information given in this report has been taken from the published abstracts rather than from the original papers. For more complete information, the original papers should be consulted.

Acknowledgments

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CLAY BINDERS

ABRASIVES (See also Grinding Wheels; Silicon Carbide.)

A Russian patent[1] described the addition of 0.25 to 0.5 percent of colloidal montmorillonite as a bonding agent to abrasive compositions that are to be molded.

ADSORBENTS

The characteristics that make fuller's earth (Florigel) suitable as a binder have been summarized,[2] and its use in making adsorbents for the petroleum industry described.

AGGLOMERATES

A French patent[3] described the addition of gels, suspensions, or emulsions of beidellite, bentonite or montmorillonite, preferably including 1 percent of $(NH_4)_2CO_3$, to materials being agglomerated. These materials—sawdust, glass wool, cork shavings, paper pulp, and wood charcoal—were then molded or pressure formed.

ALUMINA (See also Refractories and Refractory Brick.)

The use of about 10 percent of a refractory clay as a binder with bauxite, corundum, or calcined alumina (or with sillimanite) for refractory linings of equipment for steel casting is the subject of a German patent.[4]

BALL CLAYS

Ball clays have been tested for bonding molding sands;[5,6,7] Watts[7] also gave a method for determining bonding power. A ball clay was included in a study of the effects of heat on bonding.[8]

BEIDELLITE

Beidellite (a smectite) has found applications in binding various agglomerates,[3] and was among the clays studied by Gorshkov et al.[9] in regard to the effects of various electrolytes on clay-bonded molding sands. A study of the relationship between mineral constitution and bonding properties of clays[10] included beidellite.

BENTONITE

Bentonite has been more widely used as a binding agent than other clays. The types of materials in which it has found application are listed under the following headings: Agglomerates, Ceramics, Cores (Foundry), Fluorspar, Insulating Materials, Iron Ore Pellets, Molding Sand, Mucilage, Perlite, Pesticide Pellets, Pyrite and Other Sulfide Ores, Refractories and Refractory Brick, Sand, Soil, and Zeolites.

More general studies of various phases of bonding in relation to bentonite have been made. The relationship of relative proportions of clay and water to bonding applications of bentonite was mentioned by Clem and Doehler,[11] and the optimum moisture content in relation to green strength of bentonite-bonded molding sand is involved in studies by Hofman.[12] Hofmann[13] stated that hygroscopicity and heat of wetting of bentonites increased with binding properties and thus may be used as criteria for usefulness in molding sands. Hofman[12] described the improvement of green strength of bonded sand forms by treating calcium bentonites with sodium carbonate to equal the base exchange capacity. A study of Russian bentonites[14] included binding properties, and a survey of various clays from world-wide sources[15] included binding properties of bentonites.

Markhasev[16] reported that a study of five Russian bentonites, both Ca and Na types, showed no relation between their colloidality and their bonding properties.

An Italian patent[17] described the manufacture of a binding material containing 70 to 90 percent of bentonite (dehydrated at 500° to 800° C) and lime hydrate, cement, or gypsum.

Davison and White[18,19] investigated base exchange capacity, surface areas, moisture adsorption, vapor pressure at 30° C, and differential thermal analysis of various clays, including five bentonites, in relation to binding properties in molding sands, and the effects of heating from 110° to 700° C on the durability of the bonding. Hofman[20] also studied the effect of heating on bentonite bonding of molding sands and concluded that, in general, bentonites with high ion exchangeability have higher thermal resistance than those with low ion exchangeability, and that those with high initial green strength usually have a poor heat resistance. A brief explanation of the bonding action of bentonite clays was given by Vie.[21]

CATALYSTS

The use of fuller's earth (Florigel) as a binder for catalysts of the type used in petroleum processing has been described.[2]

CERAMICS

In a book that deals with the many uses of bentonite, Deribere and Esme[22] included ceramic applications. The binding property of bentonite was indicated in the improved green strength that it provided. The

properties of bentonites and montmorillonites that make them suitable for use as binders and in ceramics were given by U. Hofmann.[23] Vie[21] explained the bonding action of bentonites in various applications, including ceramics. Sukharev[1] described the addition of 0.25 to 0.5 percent of colloidal montmorillonite as a bonding agent to ceramic compositions that were to be molded, and White and O'Brien[24] found that in making lightweight ceramic block, clays containing an abundance of montmorillonite and mixed-layer clay minerals were better bonding clays than those containing only kaolinite or illite minerals. Hufnagel[25] described a Bavarian clay that was suitable as a bond for ceramic products.

CHINA CLAY

The testing of china clays as a bonding agent in molding sands has been described by Piper.[5]

COLLOIDAL NATURE

Reininger[26] proposed a theory of molding sands based on colloidal reactions that occur after mixing with water, and stated that highly swelling binding agents are superior to those that swell slightly. Magers[27] believed that colloidal clay produced a complete thin coating on each sand grain that resulted in bonding when the sand was tamped; he stated that flocculating the clay, as by the addition of a small amount of hydrated lime, increased green strength, but reduced dry strength. Markhasev,[16] however, found no relation between colloidal nature and bonding properties for the five Russian bentonites he investigated.

CORES (Foundry)

Erbsloh[28] described the use of a bentonite type of clay to which inorganic compounds, such as metal hydroxides, carbonates, chlorides, sulfates, or phosphates, were added. In the resin bonding of foundry cores, synthetic resin of the phenol-formaldehyde type may be supplemented with small amounts of bentonite.[29] The use of bentonite, illite, or other swelling clay with phenol-formaldehyde, urea-formaldehyde, or water-miscible amine-formaldehyde resin has been described by Clem.[30] On the other hand, Pelleg[31] reported that addition of bentonite to a urea-formaldehyde bonding mixture produced no significant improvement in green compressive strength, had a detrimental effect on tensile strength, but appreciably increased the hot strength of the core sand.

Pajevic and Kruspel[32] reported that a mixture suitable for cores as well as molds could be prepared from silica sand, sodium silicate, bentonite, and molasses or masut.

FERRIHALLOYSITE

Duderov and Morachevskaya[33] included ferrihalloysite clays in their study of clay-bonded graphite products.

FIRECLAY

Hofman[12] reported that the use of fireclays as binders in molding sands produced moderate green strength (between the high for bentonite and the low for illite), and that bonding strength decreased slowly on heating to 600° C. Piper[5] reported that fireclays gave adequate green strength to molding sands, but that dry strength was poor unless coal dust was added to the mixture.

FLORIGEL (See Fuller's Earth.)

FLUORSPAR

Finely powdered fluorspar, purified by flotation, has been formed into briquets of good quality and strength by using bentonite as a binder.[34] Recent work on pelletizing Illinois fluorspar fines[124] showed that satisfactory pellets for use by the steel industry could be made by incorporating 1 percent Wyoming bentonite or 1 percent of a mixture of 9 parts southern Illinois montmorillonitic clay and 1 part sodium carbonate and firing to 1700° to 1900° F.

FOUNDRY SAND (See Molding Sand.)

FUEL BRIQUETS

Clay has been recommended as an additive to pitch and crude naphthalene mixtures for bonding fuel briquets.[35]

FULLER'S EARTH

The use of fuller's earth as a binder for adsorbents and catalysts used in petroleum refining has been described.[2] Hartwell[36] discussed possible industrial uses of fuller's earth, including applications in molding sand, and Grim[37] reported that laboratory tests indicate that fuller's earth from extreme southern Illinois has definite promise as a molding sand binder. Davison and White[8,19] included fuller's earth in their studies of the effect of heat on bond life in molding sands.

GRAPHITE

The use of Indian clays as binders for graphite in making crucibles has been investigated by Prasad, Murthy, and Singh.[38] Duderov and Morachevskaya[33] studied the graphite bonding properties of ferrihalloysite, kaolinite, monothermite, and montmorillonite. Kaolinite showed lower bonding capacity and strength than monothermite; ferrihalloysite clay was characterized by high bonding capacity in the air-dry state, and strength and hardness varied little during firing from 700° to 1000° C.

GRINDING WHEELS (See also Abrasives; Silicon Carbide.)

Denninger[39] described the use of clay-feldspar-quartz bonds for silicon carbide grinding wheels and stated that mixtures of clays usually have bond strengths lower than those for either clay alone. Hufnagel[25] gave properties and analytical data for a Bavarian clay that could be used for bonding grinding wheels, and Zimmermann and Burton-Benning[40] described tests and gave physical and analytical data for different clays that could be used in this way.

HALLOYSITE

The bonding properties of halloysite for molding sands are dependent on its hydration, and attain maximum values when the clay used is a mixture of its two hydration forms (or a transition between them).[126] A comparison of molding sands bonded by several different clays showed that halloysite had about the same green compression strength as montmorillonite, but had greater compression strength than illite, which in turn had greater compression strength than kaolinite.

A comparison of dry compression strengths showed that halloysite gave lower values than montmorillonite, illite, or kaolinite, but that the halloysite-bonded sands developed greatly increased strength (air-set strength) without much loss of water when rammed specimens were allowed to dry slowly.[41] Another investigation on more fundamental properties of these clays[42] showed that reactions of halloysite and kaolinite with water were slow, and that considerable time was required for development of certain of their plastic properties.

ILLINOIS CLAYS

Grim and Schubert[43] reported on the clay minerals that occur in natural molding sands, including two Illinois sands. Grogan and Lamar[44] tested a number of Illinois clays for bonding of molding sands (see Molding Sand). Grim[37] performed laboratory tests that indicated that the fuller's earth in extreme southern Illinois has definite promise as a bonding clay for molding sand. Parham and White[45] have reported the bonding and ceramic properties of 66 Pennsylvanian clays from southern and southwestern Illinois. White and O'Brien[24] stated that Illinois clays containing an abundance of montmorillonite and mixed-layer clay minerals are better bonding clays than those containing only kaolinite or illite minerals. Jackman et al.[46,125] tested clays from about twenty locations in Illinois as binders for pelletizing Missouri iron ore, and concluded that properly prepared Illinois clays were suitable for this use. A number of these clays when treated with sodium carbonate gave pellets with green and fired strength as high as with western bentonite; dry strength was lower, but acceptable.

ILLITE

References to illite as a binder for various materials are to be found in this report under the following headings: Ceramics, Cores (Foundry), and Molding Sand.

In a study of the relation of composition to the properties of various clays, Grim[41,47,126] stated that the plasticity and bonding power produced by clay minerals decrease in the following order: montmorillonite, illite, and kaolinite.

INDIANA CLAYS

Murray[48] has tested certain Indiana clays as molding sand binders, and reported that five underclays from the western and southwestern parts of the state are potential commercial sources for bonding clays.

INSULATING MATERIALS

The properties of bentonite that make it suitable for bonding a number of substances, including insulating materials, have been given by U. Hofmann.[23] A German patent[49] described the manufacture of pressure-molded heat insulating material, consisting mainly of expanded perlite with bentonite or montmorillonite as a primary binder, and certain high molecular weight organic substances as secondary binders.

ION EXCHANGE PROPERTIES, pH, etc.

Numerous studies have been made on the relationship of binding properties of clays and such factors as their ion-exchange abilities, alkali or alkaline-earth ion contents, or pH. Grim[47] found that the green properties of clays are related to the character of the exchangeable bases carried by the clay minerals. Grim, Bray, and Bradley[10] found that the physical properties of clays varied, depending on whether sodium, calcium, hydrogen, or some other cation was present as the exchangeable ion, and that clays having a high base exchange capacity also had a high bonding strength. Endell et al.[50] and Endell[51] studied natural and synthetic molding sands, and stated that the clay in these materials is the binder, and that clays containing Na ions were superior to those with Ca ions. In other studies[51,52] they found that the shear strength of the green sand increased with increasing proportions of exchangeable bases in the molding sand, which undoubtedly means the base exchange capacity of the clay component. In molding sand tests, a montmorillonitic sodium clay with some Al replaced by Mg gave relatively high dry compressive strength, while a calcium and hydrogen montmorillonite with some Al replaced by Fe showed appreciably lower strength.[41] Endell[53] also reported that clay particles, especially those saturated with Na ions, showed a capacity for swelling, while Ca, Al, and Fe ions induced crumbling.

A French patent[28] described mold and core materials in which the binder was a bentonite-like clay to which one or more alkali metal compounds (hydroxides, carbonates, chlorides, sulfates, or phosphates) were added in an amount greater than that required for obtaining the highest swelling capacity.

In a study of the addition of lime to silica brick mixtures, Rozenblit[54] found that decreasing the CaO from between 5 to 7 percent to 3 percent made it possible to increase the clay content from 20 to 30 percent.

Makiguchi[55] found that the sedimentation velocities of suspensions of clays in water solutions were influenced by the concentration of electrolyte, and that the binding strength of clays for molding sand decreased at electrolyte concentrations that favored rapid sedimentation. Sensitivity to electrolytes apparently differs in the kaolinite type and the montmorillonite type clays.

Davison and White[19] studied the effect of heat on clays as binders for molding sand, and found that base-exchange capacity, adsorption capacity, and green strength all remained high until high-temperature dehydration occurred.

Rogers and Russell[56] investigated the sand bonding properties of New Zealand bentonites, and reported that green strength was related to clay content as measured by base-exchange capacity.

Gorshkov et al.[9] made an extensive study of five clays and twenty acid, base, and salt type of electrolytes, and found that for most of the bonds (in molding sands) activators can be found that increase the strength of the sand 1.5 to 2.0 times. The activation effect is produced by replacing certain cations in the adsorbed clay complex with others; NaOH, Na_2CO_3, and K_2CO_3 were the best activators for monothermite clay.

Hofman[12] reported that green strength of molding sands at high moisture contents could be doubled by treating calcium bentonites with an amount of Na_2CO_3 equal to the base exchange capacity of the clay, and that this reduced the rate of loss of bonding with heating but did not change the final break-down temperature. Calcium bentonites of easy base-exchange behavior may be made equivalent to natural sodium bentonites of the Wyoming type by treatment with Na_2CO_3. Hofmann[13] and Hofman[20] stated that although the bonding strength of bentonites could be correlated with heat of wetting and hygroscopicity, swelling and the calcium and sodium ion content were not related to bonding strength; yet bentonites with high ion exchangeability had a higher resistance toward loss of bonding strength upon heating than did those with low ion exchangeability.

Roberts[57] studied the effects of changing pH on the properties of natural and synthetic molding sands, and found that although additions of acids, bases, or salts changed the pH and the properties, the changes in properties were not directly related to pH but rather were primarily effected by base exchange reactions in the bonding clay.

U. Hofmann[23] mentioned cation exchange capacity as one of the characteristics of clays that makes them suitable for use in foundry sands.

Patterson, Boenisch, and Khanna[58] found that maximum green strength of foundry sands was a function of the ionic radius of the cation introduced

into the clay binder, and that the lithium ion used for activation gave maximum green strength to calcium bentonite bonded material.

Pettersson[59] studied spalling of green sand molds. He considered sodium bentonite to be the best clay, and found that additives of an acid character had a detrimental effect.

Tompkins, Spyker, and Carlson[60] produced a satisfactory foundry bond bentonite by mulling south Saskatchewan semi-swelling bentonites with Na_2CO_3.

A German patent[61] described the preparation of clay binders for molding sands by treating calcium montmorillonite with alkali or acid and adding certain activators. Hartwell[36] also discussed the use of calcium montmorillonite in its natural state and after modification by acid activation or sodium exchange.

A British patent[62] described an analogous procedure in making clay-bonded iron ore pellets, and specified that if calcium montmorillonite is used, a sodium salt such as oxalate or carbonate is added in an amount sufficient to exceed the cation exchange capacity of the montmorillonite. The resultant pellets were stronger in both green and dried states than without the ion exchange. Jackman et al.[124,125] also noted the beneficial effecting of adding sodium carbonate to clays.

IRISH BOND CLAY

An Irish bond clay was among the clays tested and found satisfactory in the preparation of synthetic molding sands.[5]

IRON ORE PELLETS (See also Pyrite and Other Sulfide Ores.)

By far the most widely used clay in pelletizing iron ore is bentonite.

Mohan et al.[63] used bentonite as one of the binders in tests of extrusion-forming cleaned iron ore from India. Jayaram, Bhuptani, and Paranjpe,[64] also in India, found that the addition of 1 percent bentonite to Naomundi ore fines being pelletized increased the durability of green pellets that were satisfactorily bonded after firing at 1250° C. Subsequently, Jayaram and Cherian[65] made satisfactory green pellets from the same fines with -65 mesh flue dust and 0.5 percent bentonite; these were then hardened at 1350° C.

A U. S. patent[66] specified the addition of 4 pounds or more of bentonite per ton of iron oxide fines to increase both green and dry strengths of pellets; further addition of 1 to 2 pounds of Na_2CO_3 per ton increased the dry strength still more.

Laboratory and pilot plant investigations of the utilization of fine ores included the pelletizing with bentonite as the binder,[67] of hematite, magnetic and non-magnetic taconite, and synthetic magnetite.

Hematite ore, ground to 75 to 85 percent -325 mesh was compressed into pellets after adding 0.5 percent bentonite;[68] these were subsequently calcined at temperatures up to 1350° C.

A German patent[69] dealing with methods of preventing abrasion of ore pellets indicated that 2.5 percent of bentonite was used in some experimental compositions, and Ross[70] has evaluated Canadian bentonite as a binder for iron ore pelletizing.

A refractory clay has been tested in Brazil for use in pelletizing powdered hematite;[71] Pinnington[62] (see Ion Exchange Properties) used montmorillonite as well as bentonite. Jackman et al. [46] tested Illinois clays from seven outcrops and found that, if properly prepared, these clays could be used for pelletizing iron ore. In general, they imparted somewhat lower green and dry strengths but greater fired strength than did Wyoming bentonite. More recent work[125] showed that better binding strength was obtained with Illinois clays by treating them with sodium carbonate.

KAOLINITE

Kaolinite has been tested and used in numerous materials as a binder. These are described under the headings Ceramics, Graphite, Iron Ore Pellets, Molding Sand, Soil, and Zeolites (see also Ion Exchange Properties).

More general studies have been carried out by Grim and Cuthbert.[41,126] Grim[47] reported that plasticity and bonding power caused by clay minerals decreased in the following order: montmorillonite, illite, and kaolinite. Grim and Rowland[72] found that the bonding power of kaolinite was lower than that of montmorillonite, but a small amount of montmorillonite added to kaolinite gave a disproportionately large increase in bond strength. Grim and Cuthbert[42] reported that the slow reaction of water with halloysite and kaolinite appeared to be responsible for the fact that there was a time lag in the development of certain plastic properties in these clays.

LACUSTRINE CLAY

A U.S. patent[73] described a molding sand bonded with a glacial-lacustrine clay containing about 14 percent CaO and 6 percent MgO.

MICA-LIKE CLAYS

Endell et al.[52] reported that the -20μ clay substance isolated from a natural molding sand (German) was principally a mica-like clay mineral with a small amount of kaolin.

MISCELLANEOUS

Watts[7] described a method of evaluating bonding power based on adding varying amounts of water, forming a 1 inch cube and observing whether it retained its cubical form when subjected to vibration for 1 minute.

Grim, Bray, and Bradley[10] reported studies on the relationship of mineral constitution of various clays to their bonding properties.

Goodison et al.[15] reported the principal characteristics, including bonding properties, of 39 clays from various sources throughout the world.

The investigations of Grim and Cuthbert[41,42,126] on behavior of certain clays in reacting with water and on comparisons of compressive strengths are cited under "Halloysite," and the investigations of Grim and Schubert[43] on Illinois molding sands, and Grim's work[37] on Illinois fuller's earth are cited under "Illinois Clays." Other work by Grim in comparing various clays[47] is given under "Illite" and "Ion Exchange Properties."

Ekdahl[74] was granted a U.S. patent on a process for making briquets of finely divided materials so that they could be charged to a melting furnace; the binder consisted of a nonswelling clay mineral, a swellable clay mineral, and gelantinized starch.

Kempcke[75] has indicated that the bonding capacity of a clay can be evaluated by determining the transverse strength of the clay with additions of 0, 50, and 75 percent of finely ground quartzite.

A French patent[76] describes a binding agent obtained by crushing and mixing a dried sandy clay with clinkers and gypsum or with portland cement.

MOLDING SAND (See also Sand.)

Richardson[6] described the use of an English ball clay to strengthen weaker molding sands and render them suitable to replace natural Belgian molding sand.

The Bavarian clay described by Hufnagel[25] could be used as a bond for molding sands.

Bentonites from Bihar, India, have been found to compare well with U.S. bentonites as binders for molding sand.[77]

There are many publications dealing with the use of bentonite as a binder in foundry molding sand. Wilson[78] gave this as the principal use of Wyoming bentonite; Freeman[79] claimed that bentonites from Manitoba and Alberta, Canada, were superior to a Wyoming bentonite. Russian bentonites are likewise used in molding sands,[80] and Italian bentonites have been compared with American for this use.[81]

Laboratory and foundry tests showed that mixtures suitable for molds for large castings (or for cores) could be made from silica sand and sodium silicate without CO_2 treatment if bentonite and molasses or masut were added.[32]

Richardson[6] used bentonite to strengthen the bonding in weakly bonded molding sands.

An adhesive for joining parts of a sand mold has been patented.[82] It consists of 12 percent bentonite, 48 percent water, 3 percent sea coal, and 37 percent curbay (a sirup residue obtained in making alcohol from molasses).

In a study of the effects of various factors on quality of test castings, Williams[83] used a molding sand bonded with bentonite and silica flour or cornstarch. The use of 1.27 percent of dry bentonite in molding sand for steel casting was reported to give improved castings that required less subsequent polishing.[84]

Tompkins et al.[60] described the beneficiation of Saskatchewan semi-swelling bentonites by mulling with sodium carbonate; the product was suitable for use in bonding molding sand. Patterson et al.[58] also studied the effect of adding sodium carbonate and other salts to bentonite for molding sands, and found that lithium gave the maximum green strength (see Ion Exchange Properties).

Vie[21] has given an explanation of the bonding action of bentonitic clays in molding sands, and discussed other uses of bentonite.

Grim and Cuthbert[41,126] suggested a bonding theory that involves coating of sand grains and the formation of "wedge-blocks" of the clay mineral between them.

Williams[85] studied the mechanism of bonding molding sands, and described the preparation of a bentonite-containing mixture that gave good results.

Barna and Juhasz[86] found that the compressive strength of bentonite-sand mixtures decreased as the specific surface of the sand grains increased.

In studies on the beneficial effects of adding 3 percent of sawdust to molding sand, Eppstein[87] used a quartz sand with 4 percent bentonite. Sawdust was found to be a better additive than bituminous coal.

Montoro[88] found that the cohesive properties of uniform molding sands were related to the ratio of moisture to bentonite.

Roberts[57] (see also Ion Exchange Properties) found that the bonding power of Wyoming bentonite was almost completely destroyed by heating at 600° C for 90 minutes.

Pettersson[59] investigated the spalling of sand molds, and mentioned a high content of clay, preferably sodium bentonite, as one of the factors contributing to good resistance to spalling; organic additives such as coal dust, cereals, or sugar were also considered important.

Kalashnikova[89] has given formulations for several molding sand mixtures for making steel castings; they contain 2 to 6 percent bentonite.

Endell and coworkers have published a series of papers on the use of clay binders in molding sands. They reported[50] that bentonites are far superior to kaolinitic clays in binding capacity and strength in both green and dried states, and that those carrying sodium ions are better than the calcium forms. Shear strength of the green sand increased with increasing proportions of exchangeable bases.[52] Another paper[51] gave properties and compositions of several clay types involved and attributed the superiority of bentonites to their high plasticity. Natural and synthetic molding sands were discussed and the American practice of using washed silica sand with bentonite was described;[90] the relationships between mechanical strength of synthetic molding sands and their bentonite and moisture contents was shown for both green and dry states.

Middleton and White[91] studied the durability of bonding capacities of clays and compared the "life" indices of bentonites; they also reported the superiority of bentonites over kaolinitic clays.

U. Hofmann[23] gave intercrystalline swelling and cation exchange capacity as characteristics of clay minerals that were responsible for their binding properties in molding sands.

Misra and Joshi[92] published data on the modulus of rupture for varying percentages of Indian (Jodhpur) bentonite in molding sands.

Feliu, Navarro, and Taylor[93] studied the bonding capacity of bentonite-water mixtures of varying composition (30 to 60 percent H_2O) between highly polished silica plates by measuring the shear stress required to cause sudden gliding and separation. They stated that the bond between bentonite and molding sand could be improved by packing to achieve higher density.

A U.S. patent[94] specified that a molding sand was made from silica sand, a small quantity of western bentonite binder, and about 10 percent olivine flour.

Dzhidzhev, Ivanov, and Angelov[95] found that mine-run Kirdzhali (Bulgaria) bentonite should be calcined at 180° to 200° C and ground to 0.42 to 0.30 mm before using it in molding sands.

Booth[96] found that the green compression strength of bentonite was related to moisture content; that low moisture corresponded to greater strength; and that variations in moisture content caused fluctuations in the properties of molding sand mixtures. He recommended 4 to 6 percent moisture for best results compatible with minimizing dust hazard.

Davison and White[19] studied the effects of loss of moisture and of heat on the life of clay bonds in molding sands. A life test in which steel foundry conditions were simulated through 4 or 5 heating cycles showed that Wyoming, Greek, and Italian bentonites retained green strength better than did Pembina and North African bentonites and natural fuller's earth, but that the reverse was true of dry strength. When water loss was small at 110° to 200° C, base-exchange capacity, adsorption capacity, and green strength remained high until high-temperature dehydration occurred; this correlation was more obvious for montmorillonitic than for kaolinitic clays. [See also Davidson and White[8]—apparently the same authors despite discrepancy in spelling—G. R. Y.]

Rogers and Russell[56] measured the sand-bonding properties of New Zealand bentonites. They found that green strength was related to clay content, and that weathering the bentonite 12 months improved its bonding properties.

Somayajulu and Nijhawan[97] reported that with Rajasthan (India) bentonite, the optimum strength, permeability, and shatter index was obtained with about 2 percent moisture for green and about 5 percent for dry sand bonding.

Dunbeck,[98] in comparing southern and western (U.S.A.) bentonites for use in molding sand in steel foundries found that southern bentonite was better for dry and hot strengths, giving higher flowability, easier shake-outs, and greater freedom from hot cracks and tears due to sand.

Hofman[12] compared various clays as molding sand binders. He found that bentonites gave the highest, fireclays moderate, and illite clays the lowest green strength. On heating, Wyoming type bentonites maintained their bonding capacity up to 600° C, kaolinites (fireclays) showed a gradual decrease, and illite clays started to break down at a little above 400° C. Green strengths of bentonite test mixtures determined at optimum moisture contents revealed little about their actual behavior in production. (See also Ion Exchange Properties.)

A book written in French[22] deals with the various industrial uses of bentonite, and includes a section on its use as a binder in molding sands.

Gorshkov et al.[9] (see Ion Exchange Properties) included beidellite, kaolinite, monothermite, and montmorillonite in the clays they tested for the effect of ion exchange on bonding characteristics in molding sands.

Dzhidzhev, Ivanov, and Angelov,[95] called attention to the fact that montmorillonite is the main component of the bentonite they used.

Some years ago Piper[5] cited the advantages of synthetic over natural molding sands, especially the better control of strength and permeability, and gave the results of tests with two china clays, three ball clays, seven fire clays, a bentonite, an Irish bond clay, and a clay recovered from natural molding sand. Only the last three gave adequate dry strength; 8 to 12 percent of china clay was required as compared to 3 percent for bentonite. The best crystallized kaolinites were least satisfactory.

Grogan and Lamar[44] have given the results of extensive laboratory tests on a number of Illinois clays, both unmodified and separated according to particle size. Their conclusions were that the Cretaceous clays tested, some residual clays, and possibly some lake clays would be suitable for foundry use in their natural state or after coarse screening, but that other clays would need beneficiation to compare favorably with commercial bonding clays.

Grim[37] reported laboratory tests that indicated a fuller's earth (a montmorillonite) from extreme southern Illinois has definite promise as a bonding clay for foundry use.

Laboratory tests on clays for foundry use have also been made with western and southwestern Indiana underclays.[48] The samples having high clay content and a rather high percentage of montmorillonite gave the best green and dry strength results, and five areas in Indiana were given as most favorable for commercial production of bonding clays.

Grim and coworkers have carried on extensive investigations of clay minerals, and a number of their reports dealt with bonding properties in relation to molding sands. Grim, Bray, and Bradley[10] studied mineral constitution of clays in relation to bonding properties, and reported that beidellite and montmorillonite gave better strength and durability than others, and that high bonding strength was shown by clays having high base exchange capacity. Grim and Schubert[43] studied the clay minerals that occur in natural molding sands and reported frequency distribution data. Green compressive strengths of 14 clays of widely different compositions were determined at 8 percent clay and 92 percent sand;[72] highest values were obtained with montmorillonite, while clays containing kaolinite and illite gave lower values. Dry compressive strengths were also investigated,[41] and found to decrease in the order: montmorillonite, illite, kaolinite, and halloysite. The relationship of water held on the surfaces of the clay minerals to bonding and plastic properties was also investigated.[42] In a paper describing methods used in clay studies, Grim[99] described the application of such studies to molding sands and clay bonding, and also discussed various aspects of the relationship of clay properties to composition.[47]

Hartwell[36] has discussed the industrial applications of fuller's earth, including those of the clay in its natural form, calcium montmorillonite, and after modification by acid activation or sodium exchange. Foundry bonding is one of the topics given special consideration.

Grimshaw and Roberts[100] used physical and chemical methods in their studies of the principal mineral constituents of kaolinite and montmorillonite types of bonding clays, and Dias Brosch[101] used electron microscopy and other physical technics in studying molding sand binders of the montmorillonite, kaolinite, and illite types.

Makiguchi[55] (see Ion Exchange Properties) investigated the effects of electrolytes on montmorillonite and kaolinite type clays used as molding sand binders.

Middleton[102] investigated the sand-bonding properties of British kaolinites and compared them with kaolinite-bentonite mixtures.

Nichols et al. [103] investigated the bonding properties of illite, western montmorillonite, southern montmorillonite (U.S.A.), and kaolinite, and drew conclusions in regard to the quality of castings produced. The castings showed little difference when sand mixtures were controlled by proper additions and kept within specifications, except that the expansion and contraction properties of the western montmorillonite and the low deformation property of the southern variety caused certain defects. Molding practices, gating and pouring, caused more defects than did deficiencies in clay properties. Roberts and Nicholas[104] have also published a report on the influence of clay content and type on the quality of iron castings.

A German patent[61] described the preparation of a highly swellable clay binder for foundry use by treating natural calcium montmorillonite with acid or alkali and using "solid compounds" as activators, and a Russian patent[1] specified the addition of 0.25 to 0.5 percent of colloidal montmorillonite as a bonding agent to ceramics, abrasives, or foundry mold compositions.

Vassiliou and White[105] made a critical examination of the relative importance of various factors in clay bonding, and studied vapor pressure and moisture characteristics of clays as related to molding sand problems. Hofmann[106] has described the use of differential thermal analysis in the study of bonding clays for molding sands.

Parkes[107] discussed the behavior of clay-bonded sands in foundry practice, and Reininger[26] described the theoretical aspects of clay bonding of sands from the colloid chemical viewpoint. He pointed out that the more highly swelling clays are superior, and claimed that his theory permits foundrymen to change the quality and properties of molding sands as desired.

Barry[73] patented a molding sand composition containing a glacial-lacustrine clay of about 14 percent CaO and 6 percent MgO content.

In a laboratory study of clay bonding, Yoshiwara[108] used spherical glass particles in place of sand, bonded them with a clay slurry, and made microscopic observations. The strength of the bonded specimen was proportional to the contact area.

MONOTHERMITE

Applications of this type of clay have been mentioned under headings "Graphite" and "Molding Sand."

MONTMORILLONITE

A number of authors have called attention to the fact that montmorillonite is the principal mineral component of bentonitic clays.[14,23,51,78,95]

Applications of montmorillonite have been listed in this report under Abrasives, Agglomerates, Ceramics, Fluorspar, Graphite, Insulating Materials, Ion Exchange Properties, Iron Ore Pellets, Molding Sand, and Soil.

Grim, Bray, and Bradley[10] studied the constitution of various bond clays, and indicated that beidellite and montmorillonite were, in general, the most suitable; Grim[47] pointed out that in many clays, the plasticity and bonding strength resulted from the presence of montmorillonite or illite minerals. Other studies of molding sands by Grim and Cuthbert[41,126] included montmorillonite.

MUCILAGE

The use of 15 parts of bentonite with 85 parts of casein to make a satisfactory mucilage has been reported.[109]

ORE BRIQUETS (See also Iron Ore Pellets; Pyrite and Other Sulfide Ores.)

A U.S. patent[110] described a bonding mixture containing marl or lime and clay; 4 to 6 percent of this was mixed with the ore to be briquetted.

PERLITE

Lightweight aggregates or insulating material may be made from suitably bonded expanded perlite. A U.S. patent[111] specified bonding with clay and firing at 1600° to 2000° F to make aggregate, and a German patent[49] described bonding with bentonite or montmorillonite plus other additives in the manufacture of insulating material.

PESTICIDE PELLETS (Granules)

The preparation of pesticides, herbicides, etc. in granular or pelletized form for more convenient and effective application to soils has been patented.[112] Certain of these formulations in which clay or bentonite was incorporated underwent disintegration at a desired rate after application.

PYRITE AND OTHER SULFIDE ORES

A British patent issued to a German firm[113] described the use of a mixture of bituminous waste sulfur and bentonite, 3 percent of which was added to flotation pyrite and the mixture pelletized. After the pellets were dried at 70° C and heated to 135° C they possessed satisfactory strength and durability. Zinc blend, antimony sulfide, and platinum concentrates could be pelletized in the same way.

Alexander[114] described the pelletizing of pyrite cinder (45 to 50 percent Fe, 14 to 20 percent SiO_2, 2 to 3 percent S) with bentonite or $Ca(OH)_2$, but found the bentonite to be the less effective.

REFRACTORIES AND REFRACTORY BRICK (See also Alumina.)

A German patent[4] described the manufacture of refractory bricks for steel casting equipment from bauxite, corundum, calcined alumina, or sillimanite, with about 2 percent H_3BO_3 and 10 percent or more of a refractory clay as the binder.

The book on bentonite[22] included material on the use of bentonite in making refractories.

The use of binding clay in refractory mortar mixes, and the plasticizing effect of calcium bentonite has been discussed.[115]

A French patent[116] gave chemical composition and physical properties of a satisfactory clay binder for refractory compositions and described the procedure involved in conditioning it to the proper moisture content.

Prasad and Murthy[117] studied the analyses and characteristics of eleven Indian clays in regard to their suitability for use in refractories.

REFRACTORY CLAY

Applications of this type of clay have been mentioned in the preceding section on "Refractories and Refractory Brick."

SAND (See also Molding Sand.)

Magers' conclusions[27] about clay bonding of sand have been summarized above under "Colloidal Nature." Barna and Juhasz[86] found that lower compressive strength of bentonite-sand mixtures resulted when the specific surface of the sand grains became larger.

Haseman[118] investigated the effects of various electrolytes on the determination of clay in 20 clay-bonded sands by the American Foundrymen's Association method, and concluded that 3 percent NaOH was the best.

Davies and Rees[119] indicated that certain British clays could be used in sand bonding to replace imported bonding clays.

SILICA BRICK

Rozenblit[54] tested various Russian clays as binders in the manufacture of lime-silica bricks and found that the optimum amount of clay

increased as the CaO used decreased; with 5 to 7 percent CaO, 20 percent clay was used, but with 3 percent CaO, up to 30 percent clay could be added.

SILICON CARBIDE (See also Abrasives; Grinding Wheels.)

Minowa et al.[120] studied the rate of erosion of clay-bonded silicon carbide brick by molten iron, and found that greater durability resulted from using smaller sized silicon carbide grains and increasing the amount of bonding clay.

Denninger's work[39] has been cited above under the heading of "Grinding Wheels."

SOIL

Peterson[121] studied the role of clay minerals in the formation of soil structure and concluded that kaolinite had little or no binding effect, but that montmorillonite was effective in forming gel-like globules of soil that had more or less resistance to dispersion in water according to the conditions of the experiment.

The incorporation of bentonite or other clay in mixtures that serve as soil binders (e.g., in road making) has been patented in India.[122]

ZEOLITES

Podorvan[123] prepared zeolite granules on a pilot plant scale using bentonite and kaolinite clays as binders.

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